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Development and Validation of a Test Method for Acrylonitrile Emissions

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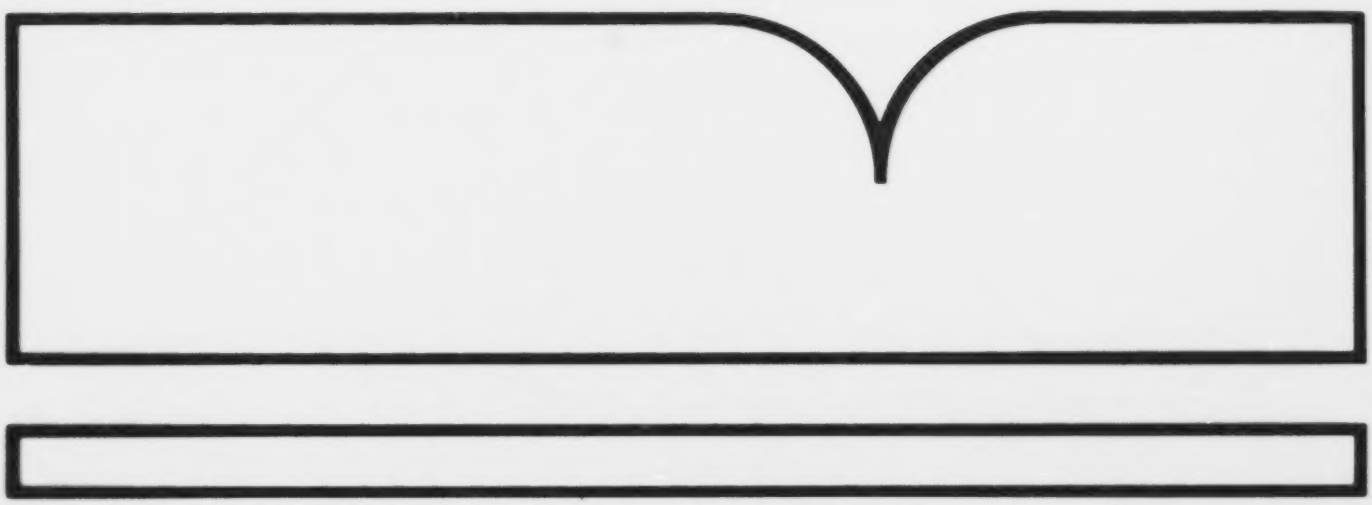

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DEVELOPMENT AND VALIDATION OF A TEST METHOD FOR ACRYLONITRILE EMISSIONS

by

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16. ABSTRACT

Acrylonitrile (AN) has been identified as a suspected carcinogen and may be regulated in the future as a hazardous air pollutant under Section 112 of the Clean Air Act. A method was validated that utilizes a midget impinger containing methanol for trapping AN vapors followed by a charcoal tube for detecting any AN lost from the impinger. The analysis was performed by capillary gas chromatography with a nitrogen selective detector. The accuracy of the method was determined to be 100 ± 4.6% from 11 tests performed in the laboratory covering the range of 10.6 to 1038 ppm AN and 0 to 40% moisture. The overall precision was 3.3%.

Field testing of the method was conducted at two different sites. The overall precision of the measured AN concentrations from simultaneous collection of samples at a nominal sampling rate of 50 mL/min over a 1-hour period was determined to be 1.86 and 2.43%, respectively, at the two field test sites. Acrylonitrile in methanol at about 35 ng/μL either with or without inhibitor was found to be stable over a 2-week period. The amount of AN in the charcoal tube samples from both laboratory and field testing was found to be less than 1% of the total amount measured in the impingers.

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems for air, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency including the Office of Air and Radiation, the Office of Toxic Substance, and the Office of Solid Waste.

Acrylonitrile is being evaluated for future emissions regulations because this compound is highly toxic and considered a cancer causing agent. Acceptable measurement methodology of these emissions from stationary sources is critical for proper assessment of the impact in the environment. Development and validation of measurement methods are key components for producing an acceptable method. This study was undertaken to perform development and validation work on a method for quantification of acrylonitrile emissions from stationary sources.

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ABSTRACT

Acrylonitrile (AN) has been identified as a suspected carcinogen and may be regulated in the future as a hazardous air pollutant under Section 112 of the Clean Air Act. This document details a laboratory and field validation of a test method for the sampling and analysis of AN emissions from stationary sources. A method was validated that utilizes a midget impinger containing methanol for trapping AN vapors followed by a charcoal tube for detecting any AN lost from the impinger. The analysis was performed by capillary gas chromatography with a nitrogen selective detector. The accuracy of the method was determined to be 100 $\pm$ 4.6% from 11 tests performed in the laboratory covering the range of 10.6 to 1038 ppm AN and 0 to 40% moisture . The overall precision was 3.3%.

Field testing of the method was conducted at two different sites. The overall precision of the measured AN concentrations from simultaneous collection of samples at a nominal sampling rate of 50 mL/min over a 1-hour period was determined to be 1.86 and 2.43%, at the two field test sites. Acrylonitrile in methanol at about 35 ng/μL either with or without polymerization inhibitor was found to be stable over a 2-week period. The amount of AN in the charcoal tube samples from both laboratory and field testing was found to be less than 1% of the total amount measured in the impingers.

This report is submitted in fulfillment of EPA Contract No. 68-02-4125 and EPA Contract No. 68-02-4442 (Entropy Environmentalists Inc./RTI Subcontract No. 1-86-4442) by the Research Triangle Institute under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from April 1987 to June 1988, and work was completed as of July 1988.

CONTENTS

Foreword iii
Abstract iv
Figures vi
Tables vii
1. Introduction 1
2. Conclusions and Recommendations 3
3. Experimental Approach and Results 5
Laboratory Evaluation 5
Equipment 5
Sample Collection and Sample Workup Procedure 7
Description of Laboratory Experiments 8
Results and Discussion 10
Field Testing and Method Validation 11
Technical Approach: Site A 12
Technical Approach: Site B 14
Results and Discussion 16
4. Analytical Instrumentation Operating Conditions and Performance Evaluation 23
Analytical System Operating Conditions 23
Analytical System Limit of Detection (LOD) and Limit of Quantitation (LOQ) 24
Analytical System Linearity 25
5. Quality Control 26
Laboratory Evaluation 26
Field Validation 26
References 29
Appendices
A. Suggested Operating Procedure for Determination of Acrylonitrile Emissions from Stationary Sources 30
B. Miscellaneous Equations and Calculations 40

FIGURES

Number		Page
1	Laboratory sampling arrangement	6
2	Site A field sampling schematic	13
3	Site B field sampling schematic	15
4	NPD chromatogram. Impinger sample from Site A (#12-C). Electrometer attenuation: 2^2	17
5	FID chromatogram. Impinger sample from Site A (#12-C). Electrometer attenuation: 2^{-2}	17
6	NPD chromatogram. Impinger sample from Site B (#1-B). Electrometer attenuation: 2^2	22
7	FID chromatogram. Impinger sample from Site B (#1-B). Electrometer attenuation: 2^0	22

TABLES

Number		Page
1	Preliminary Laboratory Experiments	9
2	Laboratory Evaluation Accuracy and Precision Tests	10
3	Accuracy and Precision Test Results	12
4	Impinger Analyses Results, Field Test Site A	18
5	Charcoal Tube Analyses Results, Field Test Site A	19
6	Validation of Results by Comparison of Two Methods of Detection: Site A Samples	19
7	Impinger Analyses Results, Field Test Site B	20
8	Charcoal Tube Analyses Results, Field Test Site B	21
9	Validation of Results by Comparison of Two Methods of Detection: Site B Samples	21
10	Linearity of NPD Response for AN over the Range 2.5 ng/μL to 1000 ng/μL	25
11	Stability Study of AN in Methanol	27
12	Analytical Recovery Results, Field Test Site B	28

SECTION 1

INTRODUCTION

Acrylonitrile (AN) has been identified as a suspected carcinogen and may be regulated in the future as a hazardous air pollutant under Section 112 of the Clean Air Act. AN has been detected in emissions from acrylic fiber manufacturing facilities and AN monomer plants. The U.S. Environmental Protection Agency (USEPA), Research Triangle Park, North Carolina, has a program to evaluate and standardize source testing methods for hazardous pollutants in anticipation of future regulations.

The Research Triangle Institute (RTI) was recently contracted by the USEPA to perform laboratory evaluation and field validation of a sampling and analysis method for AN emissions from stationary sources. A test method based upon National Institute for Occupational Safety and Health (NIOSH) Method S156 has been developed for the measurement of AN source emissions.[1] This method uses charcoal tubes to adsorb the compound during sampling, followed by solvent desorption and gas chromatographic analysis with flame ionization detection (GC/FID). EPA Method 18 is also incorporated into the procedure.[2] However, hydrocarbon interference and the presence of water vapor in the source have been detrimental to the effectiveness of the method. These factors led to a significant decrease in accuracy at low concentrations of AN when FID was utilized.[3] In this study, two modifications have been investigated in an alternative approach. The first is the use of an impinger to remove most of the water from the sample stream before it reaches the charcoal tubes. The second modification is the use of a nitrogen-phosphorous detector (NPD)[4], rather than an FID, in the analysis of the samples. The NPD was chosen for this study because it is a detector that responds selectively to nitrogen- and phosphorous-containing compounds. Generally, a very weak response is obtained with compounds that do not contain these elements. Both FID and NPD were used in the analyses of field test samples for comparison purposes. The described method was evaluated initially in the laboratory to determine the precision, accuracy, and detection limits. After the laboratory

evaluation, the method was tested at two different sites. The first field test was conducted at an acrylic fiber manufacturing plant where AN was used as a raw material. The second test was performed at an AN manufacturing facility. Samples were collected over a 2-day period at each location.

This report summarizes the various activities performed in the study. The conclusions and recommendations are described in Section 2. Section 3 contains the experimental approach and results for both the laboratory and field testing of the method. Analytical instrumentation and performance evaluation are delineated in Section 4. Section 5 outlines the quality control procedures used in the study. A detailed step-by-step sampling and analysis procedure and sample calculations and equations are included in Appendices A and B, respectively.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

Several laboratory tests were performed to determine the overall method accuracy and precision. Samples of AN at both low and high concentrations (10 to 1038 ppm) in both dry and humidified atmospheres (0 to 40% relative humidity) were collected and analyzed. Percent recovery ranged from 90 to 106% for the 11 tests performed in the laboratory. The overall average was 100 $\pm$ 4.6%. The relative standard deviation of the triplicate samples ranged from 0.6 to 9.0%. The pooled relative standard deviation of the laboratory data was determined to be 3.3%.

Field testing of the method was conducted at two different sites. The overall precision of the AN concentrations from simultaneous collection of samples (4 samples in each run and a total of 48 samples over a 2-day period) at a nominal sampling rate of 50 mL/min over a 1-hour period was determined to be 1.86 and 2.43%, for the two field test sites. AN in methanol at about 35 ng/μL either with or without polymerization inhibitor was found to be stable over a 2-week period. The amount of AN found in the charcoal tubes was less than or equal to 1% of the total amount measured in the impinger for all lab and field samples. A number of field samples were analyzed using both detectors (FID and NPD), and the results were in close agreement with each other. A few additional peaks were observed in the FID chromatograms but separated well from the AN peak under the conditions of the present study. The NPD is recommended for its selectivity and sensitivity.

The personal air sampling (PAS) pumps used in this study are generally assumed to be constant volume samplers. In actual practice, however, this may not apply in all circumstances. The pumps operate by displacement of the chamber volume with a flexible diaphragm connected to a small internal motor by a mechanical linkage. The number of pump strokes is tabulated and displayed on a counter. The mass of gas sampled is computed from the tabulated volume using the ideal gas equation. Therefore, knowledge of the chamber gas temperature and pressure is required. The principle of constant volume sampling is assumed to hold, provided that no significant flow restrictions are in the sample train. Charcoal tubes connected in line with the sample train generally offer a restriction that impedes the flow of gas to the pump chamber. Consequently, if charcoal tubes are used, the pump calibration procedure must be performed with a charcoal tube in line to obtain an accurate calibration factor.

SECTION 3

EXPERIMENTAL APPROACH AND RESULTS

LABORATORY EVALUATION

Equipment

Figure 1 is a schematic drawing of the laboratory apparatus used for the generation of AN vapor and evaluation of the impinger sampling train. The system was operated in the following manner. Concentrated AN vapor was delivered into a spherical 1-L glass mixing bulb located in an insulated, temperature-regulated enclosure and diluted with dry-grade nitrogen from a pressurized cylinder. Concentrated AN vapor was obtained from a canister prepared in the laboratory. The concentration of AN in the dilution system is determined by the relative flow rates of AN and nitrogen and the concentration of the source canister. The flow rate of both AN and nitrogen into the chamber was regulated with Tylan^{R} mass flow controllers. Moisture was introduced into the gaseous stream when necessary by bubbling the diluent nitrogen through a heated flask containing water. The moisture content in the mixing flask was controlled by the relative flow rates of the two converging streams and the water temperature in the heated flask. Three individual sample trains were connected to separate ports on the mixing chamber outlet manifold. The sample trains consisted of midget impingers and charcoal tubes connected to low-flow PAS pumps (SKC, Model 222-3).

In principle, the PAS pumps are constant volume sampling devices. The pump intake and exhaust cycle is accomplished through mechanical displacement of the pump chamber volume by a reciprocating diaphragm. The number of strokes is mechanically tabulated and displayed on a counter. The actual volume of gas sampled was calculated by applying a predetermined pump calibration factor to the tabulated number of strokes of the pump diaphragm. Calibrations were performed by determining the number of pumps strokes necessary to pull a soap bubble through a known volume. The rate of pumping

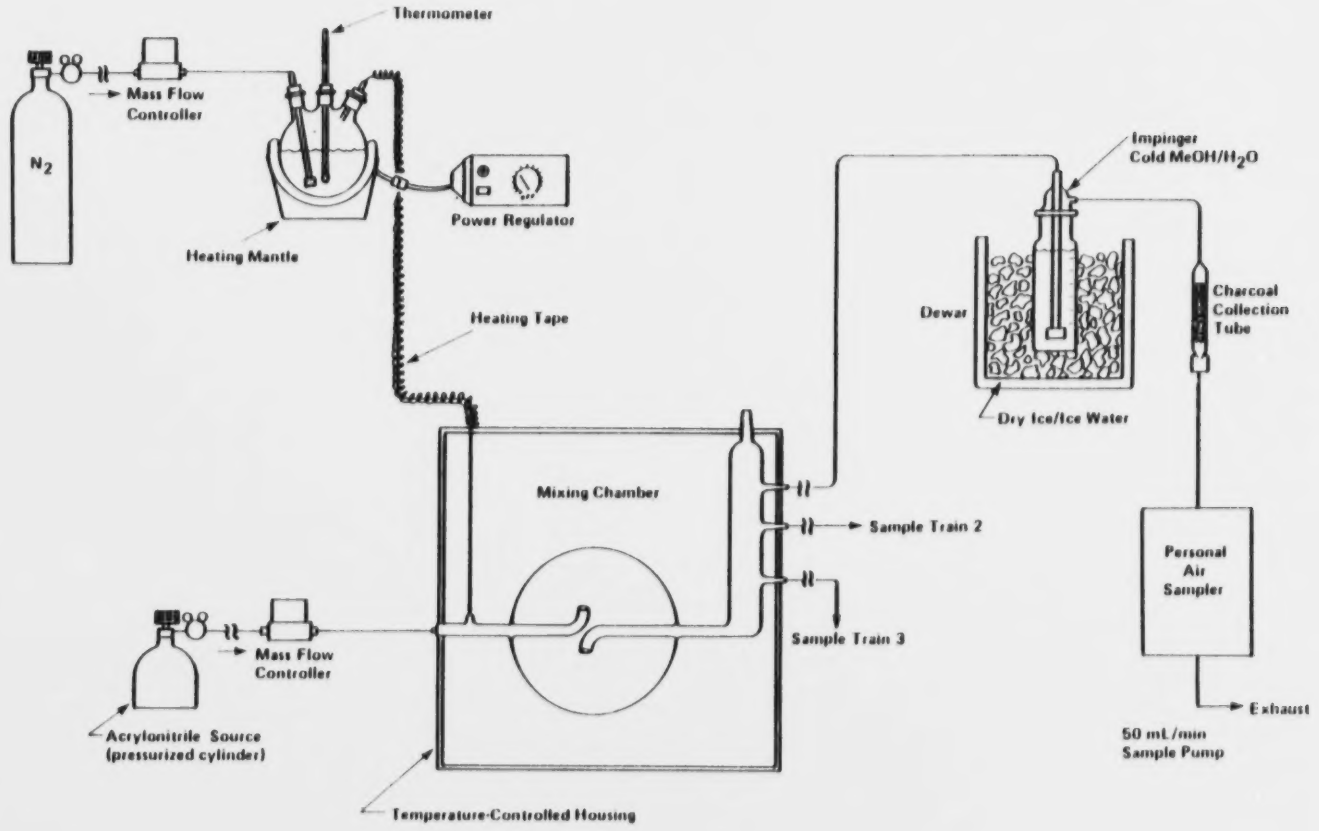

Figure 1. Laboratory sampling arrangement.

was set by an adjustment (adjustable potentiometer) on the front panel. A factor in units of milliliters/count was obtained.

The concentrated AN used in the dilution system was prepared in the following manner with a canister preparation system at RTI. A clean 6-L Summa-polished stainless steel sphere was evacuated to less than 1 mm Hg with a vacuum pump. A stainless steel sample loop of known volume connected to a high-performance liquid chromatography rotary valve was filled with pure liquid AN. The valve was rotated to the inject position where the sample was vaporized and flushed into the evacuated canister with dry-grade nitrogen. The transfer line and sample loop were simultaneously heated to ensure complete vaporization. The sphere was subsequently filled with diluent nitrogen. Pressure readings were taken with a high-precision bourdon tube gauge to within 1 mm Hg and recorded. Concentrations were calculated using the ideal gas equation and pressure measurements obtained with the pressure gauge. Equations and procedures used in the determination of canister concentrations are given in Appendix B.

Sample Collection and Sample Workup Procedure

Samples were collected using 25 mL midget liquid impingers. Impingers with either standard nozzles (1 mm opening) or sintered glass fritted tips were used interchangeably without any effect on trapping efficiency. Prior to each experiment, the impingers were filled with the appropriate solvent and placed in thermally insulated Dewar flasks containing either crushed ice, dry ice, or a NaCl/ice solution, and the temperature of the impinger solvent was allowed to reach equilibrium. A steady flow rate of gas through the dilution system was established. At a total sampling rate of 150 mL/min, excess flow of about 80 to 90 mL/min was maintained through the sampling manifold exhaust. The diluent nitrogen and AN source flow rates were measured and recorded just prior to the beginning of each experiment and again immediately afterward. Coconut charcoal tubes (SKC, Inc. 800/200 mg or 100/50 mg) were placed in line between each impinger and sample pump, and the number on the pump counter was recorded. Just prior to sampling, the impingers were connected to the manifold sampling ports with Teflon tubing and Swagelok connections. The PAS pumps were immediately turned on, and manifold gas was drawn through the impinger solutions and charcoal tubes and expelled through the pump exhaust outlets. Sampling proceeded at a rate of about 50 mL/min for 1 hour. Ambient

temperature and atmospheric pressure in the vicinity of the pumps were measured and recorded at regular intervals. At the completion of a sampling period, the pumps were switched off, and the number on the pump stroke counter of each pump was again recorded. Charcoal tubes were removed and securely capped. The impinger solutions were transferred to sample vials along with several solvent rinses and securely capped. Sample equations showing how impinger concentrations and recovery percentages were obtained from sampling data are given in Appendix B.

Impinger samples were later prepared for analysis by directly spiking each sample vial with precisely 5 μL of internal standard (valeronitrile, undiluted) using a microliter syringe. This was done just prior to sample analysis. Charcoal tubes, which were used to detect any AN lost from the impinger, were desorbed with an appropriate amount of methanol containing 2% formic acid by volume. Previous work has shown that desorption efficiency of AN is increased when 2% formic acid is used compared to methanol only.[3] The sample workup procedure is described in detail in the recommended operating procedure in Appendix A.

Description of Laboratory Experiments

Preliminary Tests--

Water and methanol were initially considered for AN collection solvents in the midget impingers. Table 1 shows a list of preliminary laboratory experiments in which the trapping efficiency of water and methanol at various temperatures was compared. The results were used to select an appropriate impinger solvent and suitable temperature for trapping gaseous AN from the source stream. Samples were collected in triplicate during each experiment according to the procedure discussed in the previous section. The table shows the temperature and solvent used in each impinger and the sequential order in which the experimental runs were carried out. The impinger recovery data and charcoal tube data are also included.

TABLE 1. PRELIMINARY LABORATORY EXPERIMENTS

Exper.	Impinger	Solvent	Temperature	Impinger % recovery	Charcoal tube recovery
I	1	Methanol	0 °C (ice)	83%	Small peak
	2	Methanol	0 °C (ice)	82%	Small peak
	3	Methanol	0 °C (ice)	84%	----
II	1	Water	0 °C (ice)	N.M.	3.9% (large peak)
	2	Water	0 °C (ice)	N.M.	3.4% (large peak)
	3	Methanol[a]	0 °C (ice)	84%	N.M.
III	1	Methanol	Ambient	77%	----
	2	Methanol	Ambient	76%	----
	3	Methanol	Ambient	78%	----
IV	1	Methanol	-14 °C NaCl/ice soln	85%	0.2%
	2	Methanol	0 °C (ice)	82%	0.4%
	3	Methanol	Ambient	74%	0.4%
V	1	Methanol	-78 °C (dry ice)	87%	No AN detected
	2	Methanol	-78 °C (dry ice)	86%	No AN detected
	3	Methanol	-78 °C (dry ice)	85%	No AN detected

N.M. = not measurable.
[a]2% formic acid in methanol.

In each of the above runs, the concentration of AN in the dilution system was calculated to be about 10 ppm. Small charcoal tubes containing 100 and 50 mg charges in the respective front and back sections were used in each run; the front sections were desorbed with 1 mL of 2% formic acid in methanol, and the back sections were desorbed with 0.5 mL of 2% formic acid in methanol. A single source AN sphere was used in each of the experiments.

Accuracy and Precision Tests--

After a preliminary determination of a suitable impinger solvent and temperature, several tests were performed to provide data for determining overall method accuracy and precision. AN samples at both low and high

concentrations in both dry and humidified nitrogen were collected and analyzed. A summary of tests performed is given in Table 2. Three samples were collected and analyzed during each run.

TABLE 2. LABORATORY EVALUATION ACCURACY AND PRECISION TESTS

Run No.	Moisture conc. (Vol.%)	AN conc. (ppm)
1	0	10.8
2	0	1000
3	30	10.7
4	20	10.6
5	30	10.7
6	33	10.9
7	32	107
8	32	101
9	32	98.6
10	37	513
11	32	1038

Results and Discussion

Preliminary Test Results--

As indicated in Table 1, water and methanol were initially considered for use in the midget sampling impingers. Source emissions frequently contain a relatively large amount of water vapor that can condense and interfere in conventional sampling and analysis methods[1,2]. In addition, AN is quite soluble in water (about 7% by volume). Therefore, water would make a very convenient solvent because of its ready availability and nonhazardous nature. However, as demonstrated by the data in Table 1, water proved to be inadequate for use in the impinger because of poor trapping efficiency and extremely low sample recovery. The amount of AN found in the impingers was below the instrumental detection threshold. Also, the presence of water resulted in poor chromatographic separations on the analytical column used for the sample analyses.

In comparison, recovery of AN from impingers containing methanol was much better. The data in Table 1 show an average recovery efficiency of about 83%

for methanol at 0 °C. As a result, this solvent was selected for further evaluation.

An appropriate solvent temperature for use in the impingers was determined from results obtained in experiments III, IV, and V. The recovery efficiency showed a direct correlation with the temperature of the impinger solution. The best results were obtained with impingers cooled with dry ice (approximately 86% recovery efficiency), while the poorest impinger recoveries were observed with those allowed to remain at ambient temperature (about 76% recovery). The recovery from impingers containing methanol at about dry ice temperatures (-78 °C) was roughly comparable to those with methanol at about 0 °C. For this reason, regular ice was considered to be preferable to dry ice for use in cooling the impingers because of its ready availability and convenience in field sampling.

Accuracy and Precision Test Results--

The results of tests performed to determine the method accuracy and precision are shown in Table 3. An average percent recovery was calculated for each run by comparing the analyzed value for each sample to the expected value. These averages ranged from 90 to 106%. An overall method accuracy can be expressed as the average percentage difference from 100% recovery. For the 11 tests performed covering the range of 10.6 to 1038 ppm AN, and 0 to 40% moisture this average was 4.6%.

The relative standard deviation of the triplicate samples ranged from 0.6 to 9.0%. An overall method precision can be expressed as the pooled relative standard deviation. For the 11 tests performed, this overall precision is 3.3%.

FIELD TESTING AND METHOD VALIDATION

Field testing of the proposed method was conducted at two different sites. The objective of the field testing was to perform a field validation of the methanol impinger and charcoal tube sampling train and to determine the precision of the method by collecting quadruplicate samples from each experimental run. The first test site was an acrylic fiber manufacturing plant (Site A). The second field test was conducted at an AN manufacturing facility (Site B). Samples were collected over a 2-day period at each location.

TABLE 3. ACCURACY AND PRECISION TEST RESULTS

Run No.	Impinger recovery efficiency, % Imp. A	Imp. B	Imp. C	Moisture conc. (Vol.%)	AN conc. (ppm)	Average percent recovery	% RSD
1	90	90	92	0	10.8	91	1.3
2	98	98	99	0	1000	98	0.6
3	93	94	95	30	10.7	94	1.0
4	95	96	97	20	10.6	96	1.0
5	90	90	91	30	10.7	90	0.6
6	95	106	100	33	10.9	100	5.5
7	100	117	101	32	107	106	9.0
8	103	102	105	32	101	103	1.5
9	105	104	106	32	98.6	105	1.0
10	99	98	98	40	513	98	0.6
11	96	95	97	32	1038	96	1.0

Technical Approach: Site A

Site A is an acrylic fiber manufacturing plant. The manufacturing process uses AN monomer in the production of acrylic polymer. AN emission from an exhaust vent at the fiber spinning and washing process was sampled over a 2-day period in December 1987. Six sample collection runs were performed on each day with four samples collected during each run. A preliminary field survey indicated that this location (fiber spinning and washing vent) had the highest emissions of two locations that were surveyed. The vent stack is one of six in a row located on the roof of the plant; it has an inner diameter of 0.8 m and is approximately 4 m tall. The sample probes were inserted through two small holes about 6 mm in diameter located in the side of the stack. All four probes were positioned to converge near the center of the stack. The sampling arrangement is shown in Figure 2. The sampling apparatus consisted of a stainless steel probe (1/8" OD x 1/16" ID) connected to a 25-mL midget impinger by about 15 cm of Teflon tubing (1/4" OD x 3/16" ID). Activated coconut charcoal tubes were connected to the impingers by another 15 cm of Teflon tubing (see Appendix A, Figure A-1). Each sample was collected over 60 minutes with a low flow PAS pump operating at about 50 mL/min. The pumps were set and calibrated in the laboratory just prior to departure to the test site.

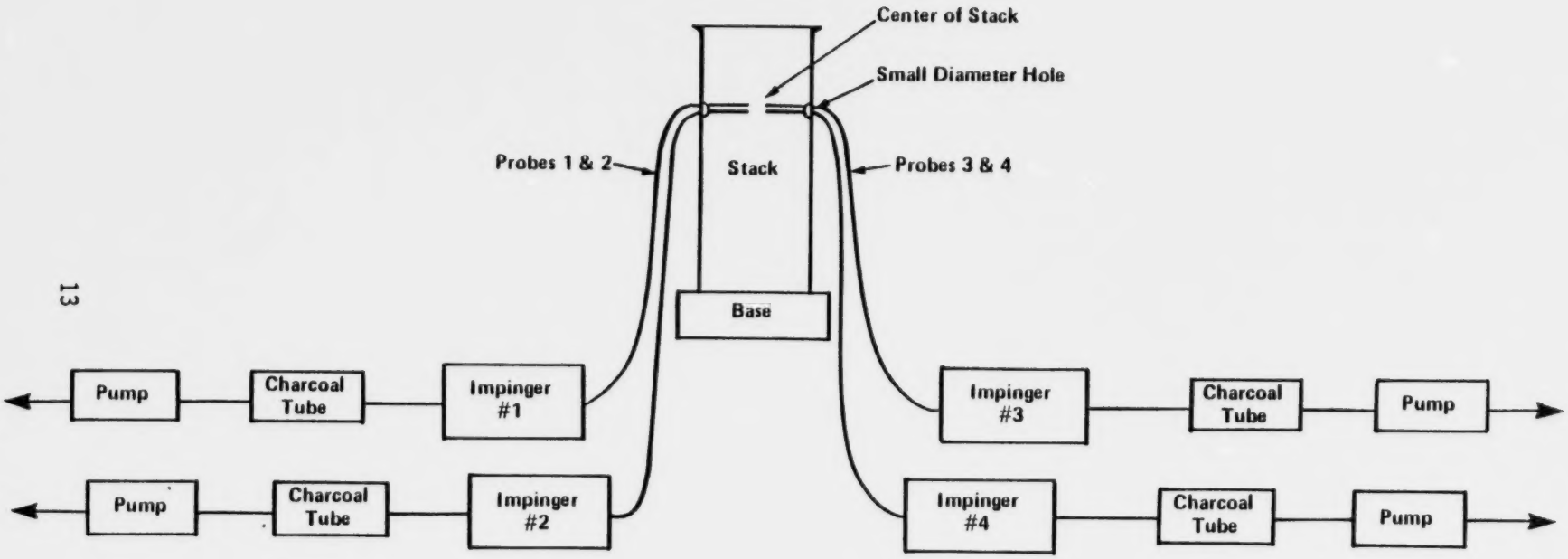

Figure 2. Site A field sampling schematic.

The impingers contained 25 mL of a solution of methanol with 36 ppm 4-methoxyphenol as an inhibitor to AN polymerization. AN was later found to be stable in methanol not containing the inhibitor, and it was not used in subsequent field testing. The impingers were placed in individual Dewar flasks and packed with crushed ice. Upon completion of each 60 min run, the impinger solutions, along with several washes, were transferred to 35 mL vials and stored on ice until they could be returned to the laboratory. The charcoal tubes were capped at the site and stored on ice, also, for transport back to the lab. Throughout the day the ambient temperature and barometric pressure was recorded for use in the final calculations. The temperature varied from 9 to 17.5 °C, and the atmospheric pressure ranged from 761 to 765 mm Hg.

The impinger samples were analyzed in the laboratory by GC/NPD. A 30 m x 0.25 mm J&W DB-WAX capillary column was used with temperature programming (60 °C [3 min] - 5 °C/min - 100 °C [1 min]) and a 60:1 injection split ratio. The instrument was calibrated against a multilevel concentration of AN containing valeronitrile as an internal standard. During the analyses, duplicate injections of each impinger sample were made with an injection of a calibration standard alternating between impinger samples.

Very little sample workup was necessary prior to analysis. The samples were prepared by adding 5 μL of internal standard, neat, directly to the vials containing impinger solution. One charcoal tube was randomly chosen for analysis from each experimental run. One hour prior to analysis, the front and rear section of each charcoal tube was desorbed individually with 8 mL and 2 mL, respectively, of methanol containing 2% formic acid and 36 ppm inhibitor. Small aliquots of these solutions were then taken for analysis and spiked with the appropriate amount of internal standard.

Technical Approach: Site B

Site B is an AN manufacturing facility. Samples were collected over a 2-day period in June 1988 from the effluent of a wet scrubber in a manner similar to that described above for Site A. An illustration of the sampling location and sampling arrangement is shown in Figure 3. The scrubber was operated under slight positive pressure. An eductor tube was used to provide vacuum, and the pinch-cock was adjusted to provide excess flow through the

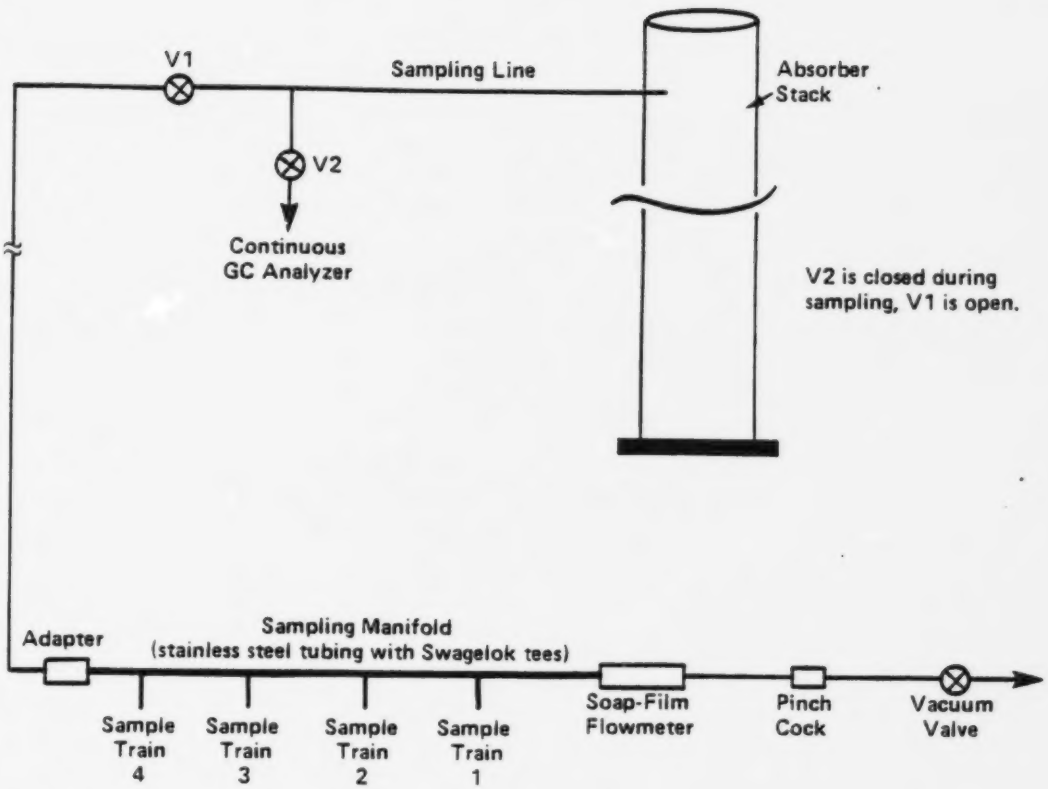

Figure 3. Site B field sampling schematic.

manifold during sampling. A soap-film flowmeter was used to check for excess flow during sampling. Instead of individual probes being used for each sample train as in the field test at Site A, each sample train was connected to a stainless steel manifold. Seven sample collection runs were performed on the first day. Six sample collection runs were performed on the second day. Quadruplicate samples were collected during each run. The arrangement of the impinger sampling trains on the sampling manifold during the first day is shown in Figure 3.

The order of the sampling train attachment to the manifold was reversed on the second day of sampling. During sampling on both days, moisture condensation was observed in the upper part of the impinger nozzles. Relatively more moisture was observed in the impingers located closest to the manifold inlet from the absorber. In general, there was an especially large buildup of moisture in the transfer line connecting the impinger to the manifold in sample #4 on the first day and #1 on the second day.

A total of fifty two 60-minute samples were collected at about 50 mL/min (except where noted). The measured temperature near the pumps ranged from a low of 13 °C to a high of 28 °C. The sample pumps were calibrated in the laboratory prior to departure with a complete sample train (probe, charcoal tube, impinger, and chilled solvent) attached to each pump.

At the end of sampling, impinger solutions and charcoal tubes were stored on either ice or dry ice until they could be returned to the laboratory and analyzed.

The impinger solutions and charcoal tubes were analyzed in the same manner as before except that a wide-bore GC capillary column was substituted for the 30 m x 0.25 mm DB-WAX capillary column. The purpose of the wide-bore column was to increase sample capacity and allow measurement of the low source concentrations that were expected by injecting a larger sample volume.

Results and Discussion

Site A--

The results of the impinger sample analyses are shown in Table 4. Source concentrations of AN were calculated according to the procedures described in Appendices A and B. Excellent method precision was achieved

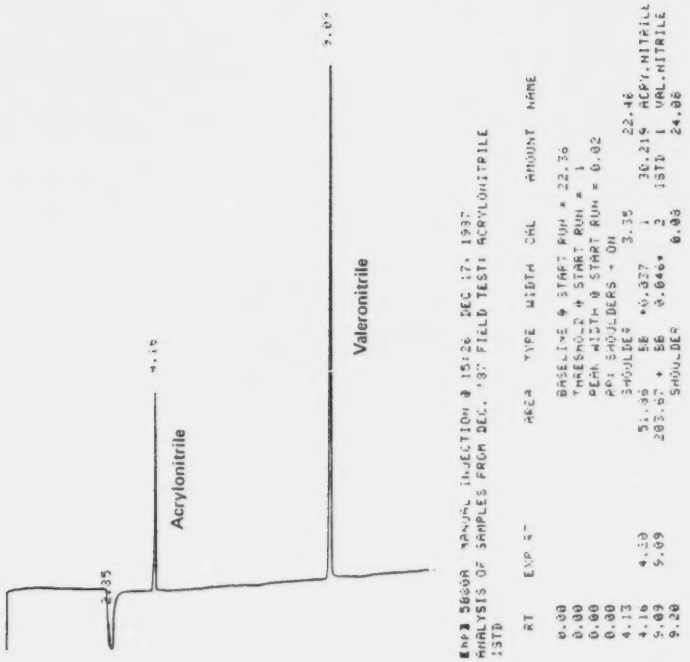

Figure 4. NPD chromatogram. Impinger sample from Site A (#12-C). Electrometer attenuation: 2^{2}.

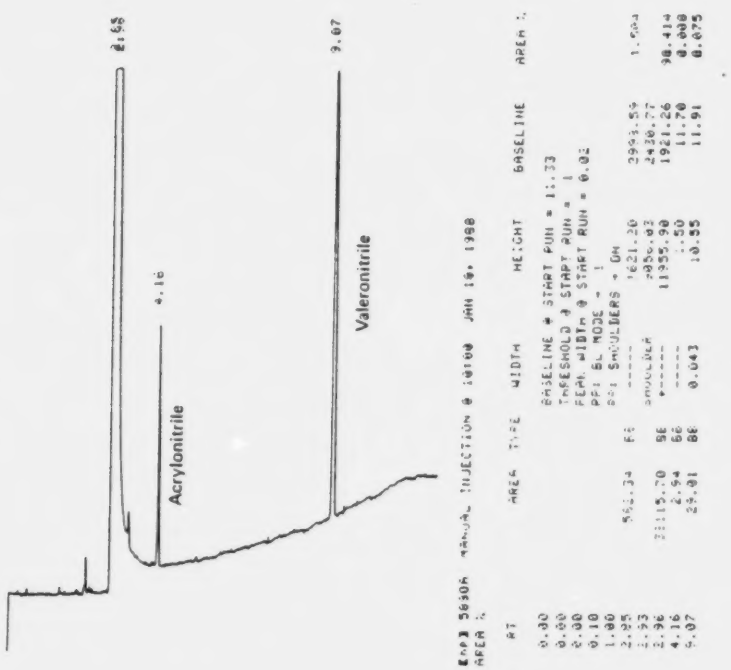

Figure 5. FID chromatogram. Impinger sample from Site A (#12-C). Electrometer attenuation: 2^{-2}.

TABLE 4. IMPINGER ANALYSIS RESULTS, FIELD TEST SITE A

	AN Source Conc. (ppm)						
Run No.	A	B	C	D	Mean	Std Dev.	%RSD
1	105	112	111	107	109	3.3	3.04
2	108	108	112	108	109	2.0	1.83
3	109	109	111	109	110	1.0	0.91
4	109	---	111	109	110	1.5	1.39
5	111	109	111	110	110	1.0	0.87
6	110	113	114	110	112	2.1	1.84
7	84.0	82.8	85.7	82.5	83.8	1.4	1.73
8	83.8	85.1	87.4	86.9	85.8	1.7	1.93
9	83.2	83.5	85.4	81.7	83.4	1.5	1.82
10	84.3	80.2	85.1	84.4	83.5	2.2	2.67
11	74.9	73.8	76.8	74.1	74.9	1.3	1.80
12	102	102	104	101	102	1.3	1.23

with the highest relative standard deviation at 3.04% for run no. 1. Linear regression of the standard deviations versus the means showed that the values were not level dependent. Application of the Bartlett test showed that the standard deviations were homogeneous. Therefore, it was possible to calculate a pooled standard deviation that was more representative of the data than the standard deviation of any single run.[5] This value was 1.8 ppm.

Data from the analysis of one charcoal tube randomly selected from each sample run are shown in Table 5. The table shows the results obtained from the front sections of the charcoal tubes. No detectable amounts of AN were found in the rear sections. The data show that the recovery in the tubes amounted to approximately 1 percent or less of the total amount measured. This agrees very well with the experimental results obtained in the laboratory evaluation.

Figures 4 and 5 are representative of chromatograms obtained from the impinger samples at Site A. The example shown is for impinger C from run no. 12. The samples from this field test were analyzed on the 30 m x 0.25 mm DB-WAX capillary column using the analytical conditions described in Appendix A. The relative sensitivity of the NPD in comparison with FID can be seen by an inspection of the electrometer settings and integrated peak areas. The response to AN using NPD is about 17 times greater than that using FID for the same sample. The analysis also shows that no significant interferences were observed in the field samples from Site A. Table 6 compares the

quantitative results obtained from samples using both NPD and FID. The analyses are in good agreement.

TABLE 5. CHARCOAL TUBE ANALYSIS RESULTS, FIELD TEST SITE A (FRONT SECTION ONLY)

Sample ID	AN conc. (ppm)
1-B	1.24
2-C	1.08
3-A	1.22
4-A	1.10
5-D	1.17
6-C	1.10
7-A	0.857
8-B	0.559
9-A	0.693
10-D	0.542
11-D	0.492
12-B	0.463

TABLE 6. VALIDATION OF RESULTS BY COMPARISON OF TWO METHODS OF DETECTION: SITE A SAMPLES

Sample	AN conc. (ppm) NPD	FID	% Difference
10-B	79.4[a]	86.3	+8.7 (+2% using average of other three NPD data)
11-B	73.3	72.7	-0.8
12-C	104.7	106.0	+1.2

[a]This number was abnormally low in the original NPD analysis. The other three impingers in this run had an average of about 84.6 ppm, which compares favorably with the FID determination for this impinger sample.

Site B--

Results of the impinger solution analyses from the second field test are shown in Table 7. A test for analytical recovery was also conducted in which a selected number of impingers were pre-spiked with AN prior to

sampling. Corrections for the spiked impingers were made by subtracting the analyzed concentration of the spiked solvent blank from the analyzed concentration of the spiked impinger samples. The spiked impingers are identified in the table and the method is discussed in more detail in Section 5. It should be noted that the sampling rate of the impinger trains in this

TABLE 7. IMPINGER ANALYSIS RESULTS,[a] FIELD TEST SITE B

	AN source conc. (ppm)						
Run No.	A	B	C	D	Mean	Std. Dev.	%RSD
1	23.2	22.5[c]	23.5	23.3[c]	23.1	0.46	2.0
2[b]	15.7	17.5		20.6	---		---
3[b]	26.3[c]	19.3	25.9[c]	25.7	---		---
4	28.3[c]	27.0	28.2[c]	27.8	27.8	0.58	2.1
5	28.0	26.5	26.0	26.7	26.8	0.86	3.2
6	27.4	26.3	26.9	27.2	27.0	0.46	1.7
7	33.6	30.6[c]	32.7[c]	33.6	32.6	1.40	4.3
8	32.9	31.5	32.9	32.3	32.4	0.65	2.0
9	38.2[c]	38.1	38.6	38.5[c]	38.4	0.27	0.7
10	43.5[c]	44.9[c]	41.5	41.3	42.8	1.74	4.1
11	42.4	41.0	42.4	41.4	41.8	0.71	1.7
12	44.1	43.4	43.6[c]	43.4[c]	43.6	0.30	0.7
13	46.6	46.0	46.6	46.0	46.3	0.32	0.7

[a]Concentrations are expressed after correction for spiked amounts.
[b]Results discarded due to problems with sampling manifold flow during sample collection.
[c]Spiked impinger sample.

field test varied considerably more than in the first field test. The actual volumes sampled on the first day (excluding run 7D) varied from about 2.2 L to about 2.9 L. Due to a low battery, the pump in sample train D in run nos. 6 and 7 operated only intermittently. The volume sampled in run no. 7D was only 0.6 L. However, in this field test, excellent precision was again achieved with the highest percent relative standard deviation at 4.3% for run no. 7. Application of the statistical methods cited in the previous section showed that the standard deviations in Table 7 (excluding run nos. 2 and 3) were also homogeneous; the pooled standard deviation was 0.84 ppm.

As before, one charcoal tube was chosen for analysis from selected sample runs. Table 8 shows the results obtained from analysis of the front sections of these tubes. No breakthrough was observed to the rear section. The charcoal tubes accounted for only about 1 percent of the total recovery.

Figures 6 and 7 are typical of chromatograms obtained with the megabore capillary column from Site B impinger samples. The figures again indicate

TABLE 8. CHARCOAL TUBE ANALYSIS RESULTS, FIELD TEST SITE B

Sample ID	AN conc. (ppm)
1-B	0.274
4-C	0.335
5-A	0.270
6-D	0.254
8-B	0.593
12-C	0.525
13-A	0.485

that the sensitivity of the FID was considerably less than the NPD. A number of additional compounds were detected in the Site B samples, none of which interfered with AN. A comparison of the two chromatograms illustrates the greater selectivity of the NPD. Quantitative results from a number of samples analyzed on both detectors are given in Table 9. The analyses are in good agreement.

TABLE 9. VALIDATION OF RESULTS BY COMPARISON OF TWO METHODS OF DETECTION: SITE B SAMPLES

Sample	AN conc. (ppm) NPD	FID	% Difference
1-C	23.5	25.0	+6.4
4-D	27.8	28.2	+1.4
8-A	32.9	32.7	+0.6
9-B	38.1	37.6	-1.3
13-A	46.6	42.0	-9.9

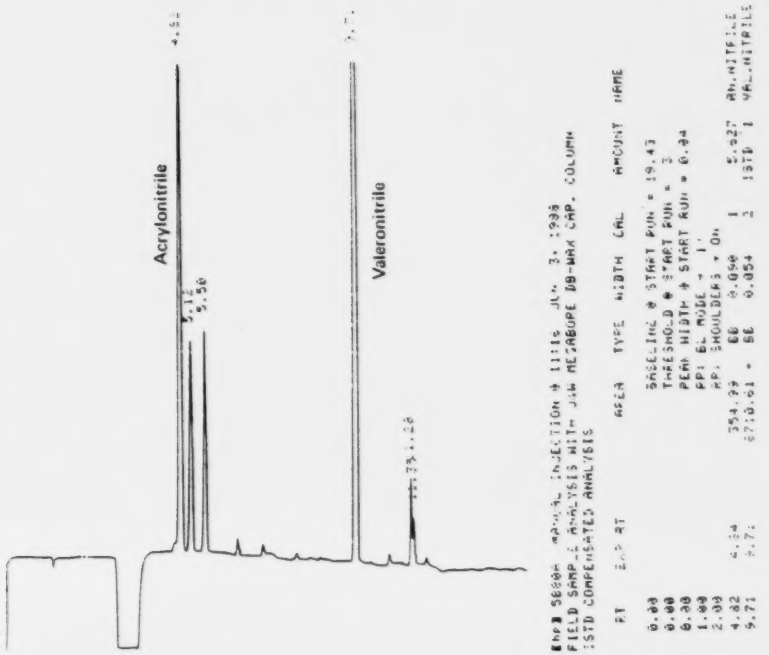

Figure 6. NPD chromatogram. Impinger sample from Site B (#1-B). Electrometer attenuation: 2^2.

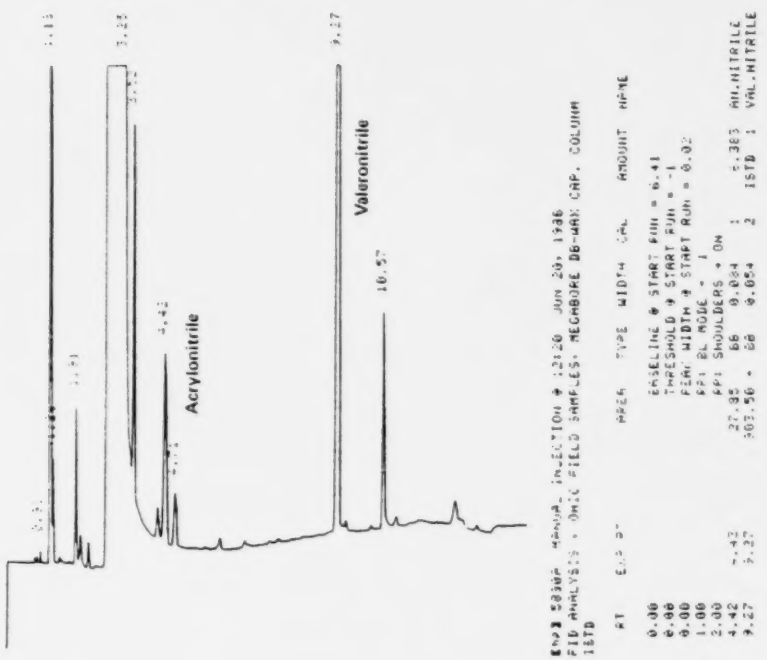

Figure 7. FID chromatogram. Impinger sample from Site B(#1-B). Electrometer attenuation: 2^0.

SECTION 4

ANALYTICAL INSTRUMENTATION OPERATING CONDITIONS AND PERFORMANCE EVALUATION

A Hewlett-Packard Model 5880A gas chromatograph with either NPD or FID detector and Level 4 integrator was used for all laboratory and field sample analyses.

ANALYTICAL SYSTEM OPERATING CONDITIONS

Samples collected during the laboratory evaluation and field test at Site A were analyzed with a Hewlett-Packard rubidium salt thermionic nitrogen selective detector and a 30 m x 0.25 mm J&W DB-WAX fused silica capillary column (0.5 μm film thickness). Helium was used for carrier gas at a flow rate of about 1.3 mL/min at 60 °C. Detector hydrogen and air were supplied at 6.5 and 85 mL/min, respectively. Helium flowing at 30 mL/min was used for makeup gas. The detector temperature was 240 °C, and the injector temperature was 250 °C. The septum purge flow was 3.5 mL/min.

Split injections of 1 μL sample aliquots were made at a split ratio of about 60:1. A glass liner in the injection port contained a flow inverter at one end and was used without glass wool packing. The column oven was programmed with the following temperature profile: initial temperature of 60 °C for 3 min, ramp at 5 °C/min up to 100 °C, and hold for 1 min. AN elutes after approximately 4 min, and the internal standard, valeronitrile, elutes at 9 min.

Samples from the field test at Site B were analyzed using a megabore capillary column and a split/splitless injection technique. The analytical column was a 30 m x 0.55 mm J&W DB-WAX fused silica capillary column (1 μm film thickness). A silanized straight bore liner was used without packing in the injection port. Typical gas flow rates were as follows: carrier helium

at 5.6 mL/min measured at 50 °C; detector H_2 and air supplied at 5 to 6 mL/min and 85 mL/min, respectively. Helium was used for detector makeup gas at a flow rate of about 30 mL/min. The injector liner was purged during the split mode with helium at about 120 to 160 mL/min. The splitless period was 1.2 seconds.

ANALYTICAL SYSTEM LIMIT OF DETECTION (LOD) AND LIMIT OF QUANTITATION (LOQ)

The single sample method[6] was used to estimate the instrumental LOD and LOQ using the standard bore analytical column and NPD. A solution of AN at a concentration of about twice the estimated limit of quantitation was analyzed nine times to determine a value for s, the approximate standard deviation at the lowest level of measurement. From this determination, the LOD is taken to be approximately equal to 3 s and the LOQ to be 10 s. The AN solution was prepared at a concentration of 0.626 ng/μL. Nine successive 1 μL injections were made at a split ratio of about 60:1. The average concentration of the nine analyses was 0.459 ng/μL with a standard deviation of 0.017 ng/μL. Thus,

$$\begin{aligned} \text{LOD} &= 3\ s\ (\text{volume injected})(\text{split ratio}) \\ &= 3\ (0.017)(1)(1/60) \\ &= 0.0009\ \text{ng} \end{aligned}$$

and

$$\begin{aligned} \text{LOQ} &= 10\ s\ (\text{volume injected})(\text{split ratio}) \\ &= 10\ (0.017)(1)(1/60) \\ &= 0.0029\ \text{ng} \end{aligned}$$

The mass detection limit for AN can also be determined in an alternative procedure from the responsivity of AN and the noise level of the NPD. The minimum detection limits are calculated by using the procedures developed by Knoll.[7] A LOD for AN of 0.5 pg, which is in good agreement with the results cited above, has been reported in previous work using this method.[4]

The minimum detectable quantity is dependent on experimental conditions of the detector bead temperature and position, nitrogen flow rate, and other instrumental parameters.

ANALYTICAL SYSTEM LINEARITY

The linearity of the NPD response was evaluated for AN over a wide range of concentrations. A standard bore capillary column was used with 1 μL sample injections at a split ratio of about 60:1. Six AN standards were carefully prepared with concentrations varying from 2.5 ng/μL (equivalent to about 10 ppm under standard sampling conditions) to 1007.5 ng/μL. The standards were prepared by serial dilution of a concentrated stock. Each solution was analyzed two to three times in sequence beginning with the low-level standard. AN response in units of peak area was recorded and is presented in Table 10.

TABLE 10. LINEARITY OF NPD RESPONSE FOR AN OVER THE RANGE 2.5 ng/μL TO 1,000 ng/μL

Nominal concentration of AN standard (ng/μL)	Mean response (in area units)
2.501	12.77
10.09	50.78
60.53	305.0
121.7	667.7
496.1	2586
1008	5250

A linear regression analysis was performed on the logarithms of the above data (log area vs. log amount). An acceptable linear response has a slope within 2% of the value one.[8] Results of the regression analyses are shown below:

Slope = 1.006
r = 0.99992

This is well within the 2% criterion.

SECTION 5

QUALITY CONTROL

LABORATORY EVALUATION

To confirm the reliability of using laboratory-prepared test mixtures for testing method accuracy and precision, two quality control tests were performed with a certified compressed gas mixture containing 15.7 ppm AN in nitrogen as the source gas. The average percent recoveries were 97% and 95%, respectively. These recoveries are in close agreement with the test results using dynamically diluted mixtures of AN in nitrogen from a laboratory-prepared canister.

During the accuracy and precision testing, two sample runs were performed with no AN added to the dilution system. One run consisted of sampling dry nitrogen and the other 30% water vapor in nitrogen. No AN was detected in the impinger solutions from these samples.

FIELD VALIDATION

Sample Stability Study--

Given the insignificant amounts of AN found in the charcoal tubes during the accuracy and precision testing, the stability of AN on charcoal is not an important consideration for this method.

A study of AN stability in methanol was performed. The level of AN studied was chosen to correspond to the amount found in the impinger samples from the first field test. Four solutions were prepared: two each with AN in methanol and inhibitor and two each with AN in methanol. The solutions were analyzed immediately, after 2 days, and then after about 2 weeks. The stability study results are shown in Table 11.

TABLE 11. STABILITY OF AN IN METHANOL

Prepared sample	Solvent	Analytical data (ng/μL)	Analysis dates
#1	Methanol	33.7	12-16-87 (Initial analysis)
		34.1	12-18-87 (After 2 days)
		34.7	12-29-87 (After 2 weeks)
#2	Methanol	33.4	12-16-87
		34.6	12-18-87
		34.5	12-29-87
#3	Methanol with 36 ppm inhibitor	33.9	12-16-87
		34.4	12-18-87
		33.8	12-29-87
#4	Methanol with 36 ppm inhibitor	34.3	12-16-87
		34.4	12-18-87
		34.9	12-29-87

The data shown indicate that AN in methanol at about 35 ng/μL, either with or without inhibitor, is stable for at least 2 weeks.

Analytical Recovery--

A test for analytical recovery from the field samples collected at Site B was conducted using the method of standard additions. In this procedure, a selected number of impingers were filled with methanol containing an amount of AN equal to 0.967 ng/μL. This is equivalent to a source concentration of about 3.7 ppm under the experimental conditions, assuming a theoretical recovery of 100%. A sample of the spiked methanol solution was retained for later comparison and analysis. Two impingers from most of the runs were spiked. The unspiked impingers contained only high-purity methanol. Analytical recovery was determined by comparing the difference between the average amount of AN collected in spiked impingers and unspiked impingers per unit of air sampled with the amount of AN added prior to sampling. The results of these measurements are shown in Table 12.

TABLE 12. ANALYTICAL RECOVERY RESULTS, FIELD TEST SITE B

Run No.	Concentration diff. (ng AN/mL air sampled)	Expected spike conc. (ng AN/mL air sampled)	%Recovery
1	10.1999	11.1455	91.5
4	14.3619	12.5940	114.0
7	10.8767	14.7909	73.5
9	11.0992	11.1221	99.9
10	17.7695	11.5987	153.2
12	12.0963	12.5466	96.4

REFERENCES

1. Eller, P.M., ed. Acrylonitrile, Method 1604 (2/15/84). In: NIOSH Manual of Analytical Methods, 3rd ed., Vol. 1. DHHS (NIOSH) Publ. 84-100. U.S. Department of Health and Human Services, Washington, DC, 1984.

2. Federal Register, EPA Method 18, 40 CFR Part 60, Appendix A, July 1985.

3. Bernstiel, T. J., M. D. Daly, A. B. Nunn, III, and L. R. Reckner. Evaluation of Charcoal Tube Adsorption for Measurement of Acrylonitrile Emissions from Stationary Sources. USEPA Contract No. 68-02-3405. Scott Environmental Technology, Inc.

4. Cooper, S. W., R. K. M. Jayanty, J. E. Knoll, and M. R. Midgett. Determination of Selected Nitrogen-Containing Hazardous Pollutants in Complex Matrices by Gas Chromatography with a Nitrogen-Phosphorous Detector. J. Chromatogr. Sci. 24: 204-209, 1986.

5. Duncan, A. J. Quality Control and Industrial Statistics, 3rd ed. Richard D. Irwin, Inc., Homewood, Illinois, 1965. P. 642.

6. Taylor, J. K., ed. Quality Assurance of Chemical Measurements, 2nd printing. Lewis Publishers, Inc., Chelsea, Michigan, 1987. P. 81.

7. Knoll, J. E. Estimation of the Limit of Detection in Chromatography. J. Chromatogr. Sci. 23: 422-25, 1985.

8. McNair, H. M. and E. J. Bonelli. Basic Gas Chromatography, 3rd ed. Varian, Inc., 1969. 306 pp.

APPENDIX A

SUGGESTED OPERATING PROCEDURE FOR
DETERMINATION OF ACRYLONITRILE
EMISSIONS FROM STATIONARY SOURCES

Formula: $H_2C=CHCN$
Molecular Weight: 53.06
Boiling Point: 77 °C
Density: 0.806 g/mL

1. PRINCIPLE

1.1. Principle. A gas sample is extracted from the effluent of the stack. The dissolved acrylonitrile (AN) is measured using a nitrogen selective thermionic ionization detector.

2. APPARATUS

2.1. Sampling. The sampling apparatus is shown in Figure 1. Component parts are described below. The method specifies a sampling rate of 50 mL/min over a 1 hour period with samples collected in replicates of four or more.

2.1.1. Probes. Stainless steel, 1/8 inch outer diameter, 15-20 feet in length.

2.1.2. Impingers. One 25 mL midget impinger per probe. Impingers with either glass frits or standard tips may be used.

2.1.3. Tubing and Interconnections. TFE Teflon tubing, 1/4" OD x 3/16" ID x 1/32" wall. About 5 inches is needed for each impinger inlet and outlet. Teflon Swagelok unions and fittings, 1/4", are required for all direct connections to the

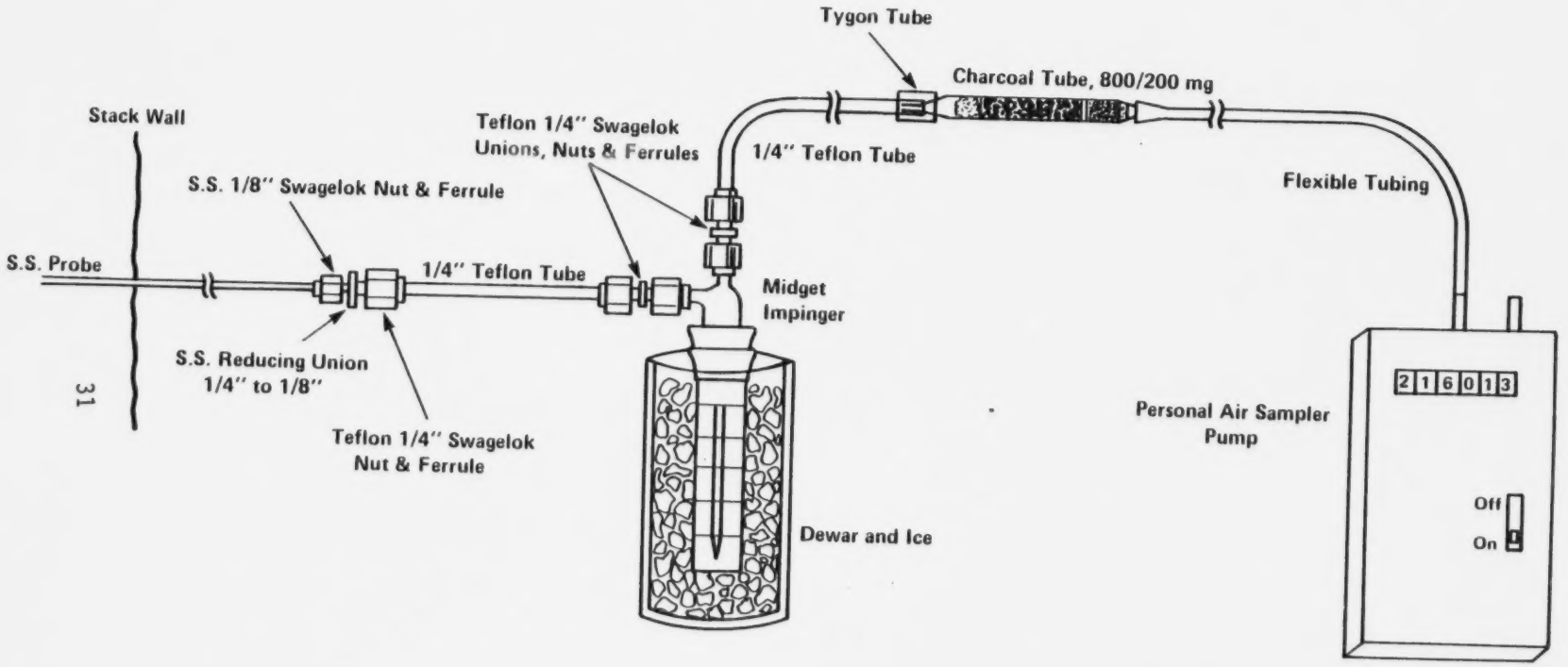

Figure A-1. Acrylonitrile sampling apparatus.

impingers. The probe must be connected to the impinger inlet line with a 1/8" to 1/4" stainless steel reducing union with 1/8" nut and ferrule on the probe and 1/4" Teflon nut and ferrule on the impinger inlet tube.

2.1.4. Sorbent Tubes. 800/200 mg coconut charcoal. Sorbent tubes must be connected to the impinger outlet with a short length of Tygon tubing (about 1 inch) in such a manner that the tip of the charcoal tube extends snuggly into the end of the Teflon tube. The Tygon tube has an inner diameter just large enough to allow it to be placed simultaneously over the outside of the impinger outlet and the charcoal tube without slipping off or leaking.

2.1.5. Pump. Diaphragm pump with flow rate adjustable from 50-200 mL/min. Pump must be a constant volume sampler with a pump stroke counter.

2.1.6. Mercury Thermometer. For measuring ambient temperature. Temperature of gas exiting pump chamber is assumed to be at ambient temperature (a good approximation).

2.1.7. Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure within 1 mm Hg. In some cases, the barometric pressure may be obtained from a nearby National Weather Service station. Corrections for differences in elevation between the weather service station and sampling location may be applied at the rate $\pm$ 2.5 mm Hg per $\pm$ 30 m difference in elevation.

2.1.8. Dewar Flasks. Thermally insulated Dewar flasks sufficiently large (about 350 mL) to accommodate impinger and crushed ice.

2.2. Sample Recovery.

2.2.1. Storage Bottles. Glass vials, 35 mL, for each impinger sample. Vial caps must be lined with Teflon.

2.2.3. Disposable Pasteur Pipets. 5 3/4 inch borosilicate glass pipets with bulbs for solvent rinsing of impingers.

2.3. Analysis.

2.3.1. Standard Vials and Flasks. Glass vials, 1.7 - 2.0 mL, with Teflon-lined caps. Class A volumetric microflasks, 1 mL ($\pm$ 0.01 mL) and 5 mL ($\pm$ 0.02 mL), for preparing calibration

standards.

2.3.2. Sample Vials. Glass vials with Teflon caps for use in extracting sorbent tubes. 10 mL vials are needed for front section, 5 mL vials are needed for backup section. See also Sections 2.2.1. and 2.3.1.

2.3.3. Microsyringes. Appropriately sized syringes, 5 μL and 100 μL, for use in preparation of calibration standards and samples for analysis.

2.3.4. Gas Chromatograph.

2.3.4.1. Column and Injector. Wall-coated J&W DB-WAX capillary column, crosslinked and bonded. Column temperature program: 60 °C (hold 3 min), 5 °C/min to 100 °C (hold 1 min). Column dimensions: 30 m x 0.25 mm, 0.5 μm film. Carrier gas: 1.3 mL/min measured at 60 °C. Split mode of injection using microliter syringe with 2" needle into wide-bore (4 mm) glass liner with flow inverter near the end. Liner is used without packing material. Split ratio: approximately 60:1. Injector temperature: 250 °C. Alternate analytical column: DB-WAX wide bore capillary column, crosslinked and bonded. Column temperature program: 50 °C (hold 4 min), 8 °C/min to 110 °C (hold 3 min). Column dimensions: 30 m x 0.55 mm, 1μm film. Carrier gas: 5.6 mL/min measured at 50 °C. Split/splitless mode of injection; splitless period 1.2 seconds followed by helium purge at 120-160 mL/min. AN elutes after about 4 min and the internal standard after about 9 min.

2.3.4.2. Detector. Flameless thermionic nitrogen/phosphorous selective detector uilizing an electrically heated bead containing rubidium salt positioned just above the detector jet with a low H_2/air ratio. Detector sensitivity and stability is highly dependent on bead temperature and its relative position above the jet. Make adjustments as necessary to obtain the optimum sensitivity and stability. Detector temperature: 240 °C. Detector hydrogen: 6.5 mL/min. Detector air: 85 mL/min. Makeup gas: helium at 30 mL/min.

3. REAGENTS

The highest purity reagents should be used, particularly in the preparation of calibration standards.

3.1. Sampling.

3.1.1. Methanol. Capillary GC grade methanol for use as impinger solvent. Each impinger shall be filled with 25 mL of solvent. Allow an additional amount for rinsing and quantitative transfer of sample to storage vials.

3.2. Sample Recovery.

3.2.1. Methanol with 2% formic acid. A prepared solution of capillary GC methanol containing 2% v/v formic acid for use in extracting charcoal tubes.

3.3. Analysis.

3.3.1. Acrylonitrile. The highest purity available (Aldrich, 99 + %) for use in preparation of calibration standards. Shall contain 35-45 ppm 4-methoxyphenol to inhibit AN polymerization.

3.3.2. Valeronitrile (M.W. 83.13, b.p. 139-141, d. 0.795). Very high-purity valeronitrile (Aldrich, 99%) to be used as an internal standard in the samples during laboratory analysis.

3.3.3. Helium. Ultra-high purity for GC carrier gas and detector makeup gas.

3.3.4. Hydrogen. Ultra-high purity for nitrogen-phosphorous detector (NPD).

3.3.5. Air. For NPD, filtered.

4. PROCEDURE

4.1. Sampling.

4.1.1. Preparation of Sampling Apparatus. Position sampling probe within effluent stream near the center of the stack. Secure probe to prevent movement. Fill impinger with 25 mL of clean methanol; place in Dewar flask and surround with ice. Allow sufficient time before sampling for solvent to reach approximately 0 °C. Score both ends of each charcoal tube and break the tips. Attach one end to the impinger tubing and the other end to the pump tubing. Connect impinger inlet line to the sampling probe by means of a reducing union and Swagelok fittings

(see Section 2.1.3.). Securely tighten all joints to eliminate any possibility of leakage and inspect during sampling to ensure good leak-free connections.

4.1.2. Sample Collection. Record the ambient temperature in the vicinity of the pumps, the atmospheric pressure, initial count on the pump meter, and the temperature of the stack gas. Connect the probes to the impingers, turn on each pump, and begin timing. Record the temperature and pressure after 30 min and at the end of the run. After 1 hour of sampling, turn pumps off and record final count on the pump meter.

4.1.3. Sample Recovery. Disconnect the impingers from the probes. Remove charcoal tubes, cap the ends tightly, and label. Pour the contents of the impingers into individual sample storage bottles. Rinse each impinger three to four times with clean methanol, and add the washings to the sample storage bottles. Seal tightly and label each. Place charcoal tubes and sample bottles in an insulated chest with ice.

4.2. Sample Preparation.

4.2.1. Impingers. Remove from cold storage only the samples to be analyzed that day. Spike exactly 5μL of pure, undiluted valeronitrile directly into each sample solution and invert container several times to mix thoroughly.

4.2.2. Sorbent Tubes. Remove from cold storage only the charcoal tubes to be extracted that day. Score glass and break open tube discarding the foam and glass wool. Transfer the front section charcoal (800 mg) and the backup charcoal (200 mg) to 10 mL and 5 mL vials, respectively. Add precisely 8 mL of methanol containing 2% formic acid to the front section charcoal and 2 mL to the backup charcoal. Desorb for about 1 hour with occasional agitation.

4.3. Sample Analysis.

4.3.1. Impingers. Inject duplicate 1 μL aliquots of each impinger solution into a calibrated gas chromatograph. Bracket each set of duplicate injections with a standard injection at a concentration comparable to that found in the samples. Repeat

this pattern for all samples to be analyzed. Plot the chromatograms and collect the integration data for later analysis.

4.3.2. Sorbent Tubes. Transfer 490 μL aliquots of the charcoal tube extracts to small vials (1.7-2.0 mL capacity). Add to each sample vial precisely 10 μL of internal standard diluted 1:100 according to Section 4.4.3, and mix thoroughly. Make replicate injections in the manner as described above (Section 4.3.1.). Plot chromatograms and collect the data.

4.4. Calibration.

4.4.1. Pump. Set pumps to a sampling rate of 50 mL/min. Attach a complete sample train (sample probe, impinger containing methanol solvent placed in Dewar with ice, and charcoal tube) to each pump. Calibration is made using a soap-film flowmeter or other appropriate device. This is accomplished by determining the number of pump strokes needed to pull the soap film through an accurately known volume (100 mL is convenient). Calculate a pump factor, mL/count, for each individual pump. The calibration of pumps should be conducted within a few days prior to their intended use with fully charged batteries. Only pumps that are known to be reliable should be used in field sample collection.

4.4.2. Gas Chromatograph. A multilevel calibration of the GC is performed using the internal standard method and a series of solutions of AN at known concentrations. The internal standard, valeronitrile, is spiked into the standard solutions to give a concentration of 159 ng/μL. The AN standards are prepared volumetrically at concentrations of 316 ng/μL, 29.3 ng/μL, and 2.99 ng/μL.

4.4.3. Preparation of Standards. All three standards shall have a total volume of 1000 μL each. This or a similar recipe should be followed each time a fresh series of calibration standards is prepared. Care must be taken to ensure accuracy and consistency of technique when measuring and adding liquid volumes. When using the pure liquids, they should be at about the same temperature (20 °C) on each occasion to ensure consistent density

from one use to another. Prepare stock solutions of AN and valeronitrile. Valeronitrile (1:100 dilution): To a 1 mL class A volumetric microflask (± 0.01 mL), add 10 μL of undiluted valeronitrile and dilute with methanol to 1 mL (7950 ng/μL final conc.). AN (1:2500 dilution): To a 5 mL class A volumetric microflask (± 0.02 mL), add 2 μL of undiluted AN and dilute with methanol to 5 mL (322.4 ng/μL final conc.). Prepare three levels of calibration standards. High level: Add 980 μL of AN stock solution to a small vial (1.7-2.0 mL). Add 20 μL of the internal standard stock solution to give a final concentration of 316 ng/μL. Mid-level: To another small vial add 100 μL of AN stock solution and 980 μL of methanol. Transfer 100 μL of this mixture to a third small vial to be used for the low-level calibration standard. Add 20 μL of internal standard stock solution to give a final concentration of 29.3 ng/μL. Low-level: Complete the low-level calibration standard by adding 880 μL of methanol and 20 μL of internal standard stock solution. Final concentration is 2.99 ng/μL.

5. CALCULATIONS

5.1. Field Data. Calculate the number of moles of air sampled:

$$n_1 = \frac{P_A V}{P_S T_A R} \qquad \text{Eq. 1}$$

Where: n_1 = Number of moles of air sampled.
V = Volume of air sampled, liters.
P_S = Standard pressure, 760 mm Hg.
P_A = Average ambient pressure during sample collection, mm Hg.
T_A = Average ambient temperature during sample collection, °K.
R = Gas constant, 0.08206 L atm/°K mol.

5.2. Laboratory Data. Calculate the number of moles of AN collected

$$n_2 = \frac{C_1 V_1 + C_2 V_2}{M.W.} \times (10^{-9}) \qquad \text{Eq. 2}$$

Where: n_2 = Number of moles of AN collected.
V_1 = 25,000 μL (impinger samples).

V_2 = 8,000 μL (charcoal tube samples).
C_1 = Impinger sample concentration, ng/μL.
= R_i C_i
C_i = Measured concentration in impinger sample, average of the replicate determinations.
R_i = (Prepared conc. of calibration standard)/(measured conc. of calibration standard); the measured concentration of calibration standard is taken to be the average of two determinations that bracket C_i.
C_2 = Charcoal tube, concentration in desorbing solution, ng/μL.
= $R_{ii}C_{ii}$
C_{ii} = Measured concentration of desorbing solution.
R_{ii} = (Prepared conc. of calibration standard)/(measured conc. of calibration standard); the measured concentration of calibration standard is taken to be the average of two determinations that bracket C_{ii}.
M.W. = Gram molecular weight of AN, 53.06 g/mole.

Notes :

The individual calibration factors are necessary due to daily variation (usually minor) in the response of the instrument to AN in relation to its response to the internal standard, valeronitrile.

The internal standard method of calibration and analysis permits precise measurements to be made by internally compensating for variation in the injected volume of sample aliquots and for subtle changes in the split ratio (but not changes in relative response as mentioned above). In addition, this method eliminates the need to know the precise liquid volume of the samples, provided that they are properly spiked with internal standard solution.

The values for V_1 and V_2 are derived from the manner in which the sample is prepared for analysis and the way in which the instrument calibration is performed. For example, the system is calibrated by analyzing a prepared mixture containing valeronitrile at 159 ng/μL and AN at some nominal level. (A calibration curve for AN is generated internally by the integrator based on the response of the detector to AN at the prepared concentration.) The impinger samples are assumed to contain exactly 25 mL of liquid. The actual volume may differ

from this. A sufficient amount of valeronitrile is then added to this assumed volume to give an apparent concentration of 159 ng/μL (i.e., 5 μL of undiluted valeronitrile, density 0.795 g/mL). The integrator assumes that all samples will be spiked with internal standard to that concentration. When a sample is analyzed, a comparison is made between the response to the internal standard in the sample and the response for the internal standard when the calibration was performed. If there is any difference between the sample and the standard, a factor is applied to the internal standard in the sample to make it agree with the calibration standard. This factor is applied likewise to the response obtained for the AN in the sample. Thus, even though the reported concentration is not necessarily the true concentration, it is the concentration that would be present if the sample volume was at exactly 25,000 μL. Therefore, the volume in Equation 2 is 25,000 μL for V_1. The same reasoning can be applied to the 490 μL aliquots of the charcoal tube extracts, and the volume in Equation 2 is 500 μL for V_2.

5.3. Source Concentration. Calculate the AN source concentration:

$$C_s = (n_2/n_1)\ 10^6 \qquad \text{Eq. 3}$$

Where: C_s = AN source concentration, ppm.

5.4. Statistical Treatment. The data for each sample set is used to determine the precision of the samples by calculating the relative standard deviation of the measurements within that particular sample set:

$$\%\ RSD = (s/x)\ 100 \qquad \text{Eq. 4}$$

Where: RSD = Relative standard deviation of sample set results.
s = Standard deviation of sample set data.
x = Average concentration of sample set.

APPENDIX B

MISCELLANEOUS EQUATIONS AND CALCULATIONS

CANISTER STANDARDS FOR LABORATORY EVALUATION

Source canisters containing acrylonitrile (AN) vapor were prepared on a canister preparation system consisting of a high-pressure nitrogen source (approx. 2300 torr), a vacuum pump, a precision bourdon tube gauge (Heise), a 6-port HPLC rotary valve, a stainless steel capillary sample loop, and associated fittings, tubing, and accessories. The canister is connected to a vacuum or N_2 pressure source through a path consisting of stainless steel tubing and appropriate valves and tees. Pressure within the system is monitored with the bourdon tube gauge. The sample loop may be switched into or out of the flow path by rotating the HPLC valve. Turning the rotary valve to the load position allows for filling the sample loop with pure AN liquid. Turning the rotary valve to the inject position establishes flow of nitrogen at a preset rate through the loop and into the evacuated canister. Exposure of the liquid to a vacuum together with heat applied to the loop and transfer line ensures that the sample is completely vaporized. After the sample is transferred, the canister is fully pressurized with nitrogen. The mixture is then diluted by withdrawing a portion of the gas and refilling the canister with clean nitrogen. The AN concentration within the canister is calculated from the following equation.

$$ppm = \frac{(V\ liq.)\ (D\ liq.)\ (24.45)\ (760\ mm\ Hg)\ (T\ amb.)\ (1000)}{(V\ can)\ (M.W.)\ (P\ can)\ (298\ ^{o}K)} \qquad \text{(Eq. 1)}$$

where: V liq. = volume of AN injected (μL)
D liq. = density of AN (g/mL)
24.45 = molar volume at 760 mm Hg and 298 K (L/mole)
T amb. = room temperature (^{o}K)
V can. = volume of canister (L)
M.W. = molecular weight of AN (g/mole)
P can. = pressure, absolute, within canister (mm Hg)

An example showing the calculation of AN concentration in a typical canister standard is given below:

Data: atmospheric pressure = 758.1 mm Hg
room temperature = 25 °C
volume of AN injected = 12.4 μL
internal volume of canister = 6.09 L
density of AN = 0.806 g/mL
molecular weight of AN = 53.06 g/mole
initial pressurization to: 2984 torr (absolute)
partial evacuation to: 721 torr (gauge)
final pressure after dilution: 2998 torr (absolute)

Substituting this data into eq. 1 yields:

$$ppm = \frac{(12.4\ \mu L)(0.806\ g/mL)(24.45\ l/mole)(760\ mm\ Hg)(298\ K)(1000)}{(6.09\ L)(53.06\ g/mole)(2984\ mm\ Hg)(298\ ^{o}K)}$$

$$= 192.6\ ppm$$

The dilution factor is:

$$\frac{(\text{Pressure in partially evacuated canister}) + (\text{Atmospheric pressure})}{(\text{absolute final pressure})} \quad \text{(Eq. 2)}$$

or

$$\frac{(721\ torr) + (758\ torr)}{(2998\ torr)} = 0.493$$

The final tank concentration is therefore:

$(192.6\ ppm)(0.493) = 95.0\ ppm$

PERCENT RECOVERY IN LABORATORY IMPINGER SAMPLES

Recovery in the laboratory sampling trains was calculated from the following equation. The equation below was used to determine the amount of AN expected in the impingers assuming 100% recovery efficiency:

$$\frac{(C)(V)(P)(M.W.)(10^{-6})}{(R)(T)(10^{-9})(25{,}000\ \mu L)} = ng/\mu L \quad \text{(Eq. 3)}$$

Where: C = concentration of AN in sampling manifold (ppm)
V = volume of gas sampled (L)
P = atmospheric pressure in vicinity of pumps (atm)
M.W. = molecular weight of AN (g/mole)
R = gas constant (0.08206 L atm/K mole)
T = temperature in vicinity of pumps (^{o}K)

The collected impinger samples were analyzed on a GC calibrated with AN standard at a concentration (ng/μL) similar to that expected in the samples. Ideally, a fresh calibration mixture should be prepared after 1-2

days of use because degradation has been observed over this time period in low-level standards (2-3 ng/μL). There is some variation in NPD response both during and between days, and this is taken into account by applying a multiplication factor to the reported concentration of the calibration standard and the measured concentration (see Appendix A, Eq. 3) The percent recovery in the impinger samples was calculated by comparing the concentration in the impingers determined by analysis with the expected concentration for 100% recovery obtained from Eq. 3 above.

MOISTURE CONCENTRATION

The moisture content generated in the sampling manifold during the laboratory evaluation was determined from the following equation:

$$V_{\%} = \left(\frac{P_V}{P_A}\right)\left[\frac{\frac{F_D}{\left(1 - \frac{P_V}{P_A}\right)}}{\frac{F_D}{\left(1 - \frac{P_V}{P_A}\right)} + F_T}\right](100) \qquad \text{(Eq. 4)}$$

where: P_V = vapor pressure of water at temperature of flask (mm Hg)
P_A = atmospheric pressure (mm Hg)
F_T = flow rate from AN tank (mL/min)
F_D = dry flow rate of moisture stream (mL/min)
$V_{\%}$ = moisture content of manifold by % volume

Solving this equation for P_V yields the following:

$$\frac{P_A V\ (F_D + F_T)}{100\ F_D + V F_T} = P_V \qquad \text{(Eq. 5)}$$

Thus, at given flow rates of N_2 and AN standards ($F_D + F_T$), the vapor pressure of water at various target levels of moisture can be calculated. The temperature needed in the heated flask can then be obtained from vapor pressure tables for water.